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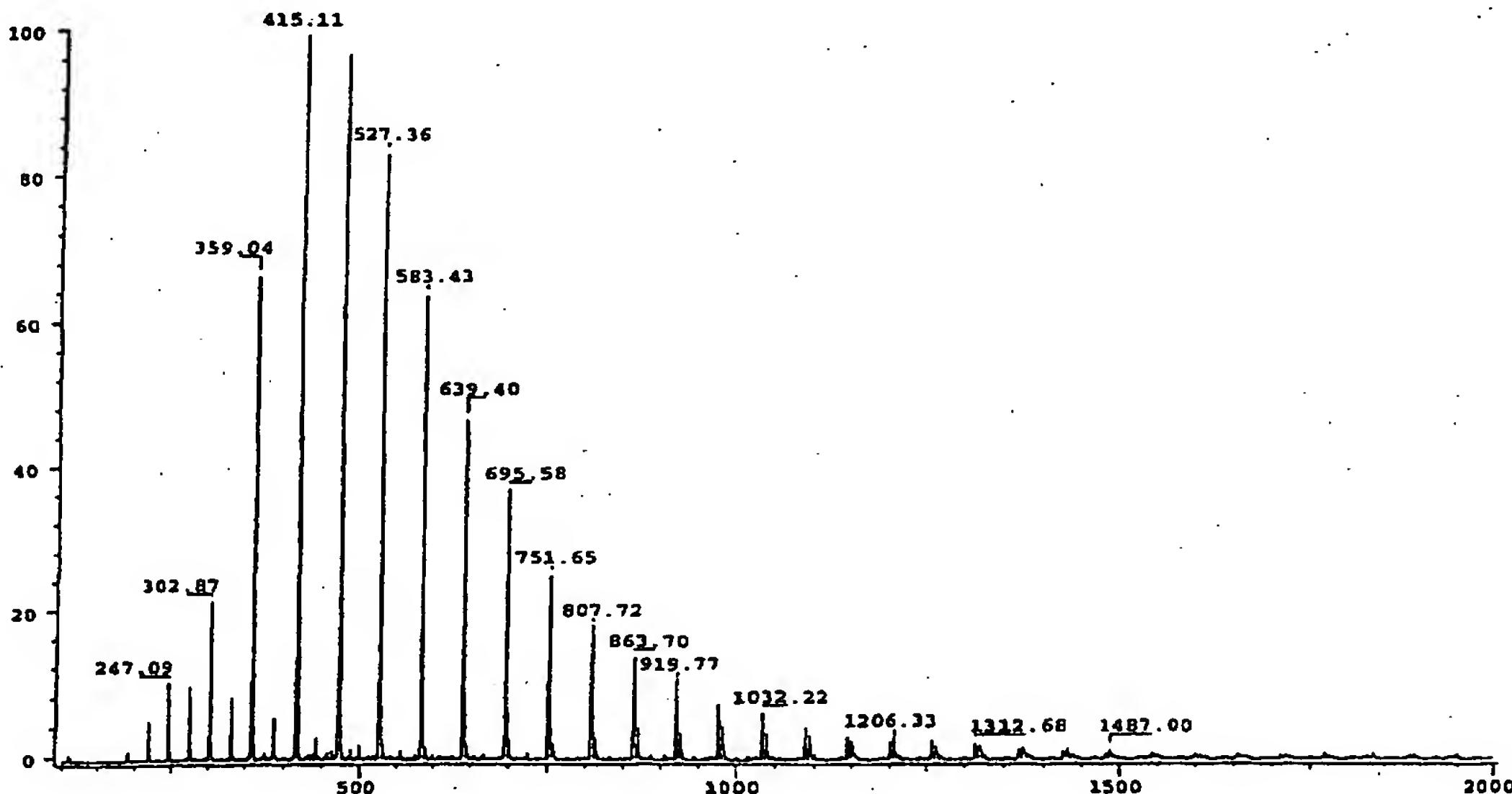
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(54) Title: POLYALKENYL SULFONATES



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(57) Abstract: Provided is a polyalkenyl sulfonic acid composition comprising a mixture of polyalkenyl sulfonic acids derived from a mixture of polyalkenes comprising greater than 20 mole percent alkyl vinylidene and 1,1-dialkyl isomers, and a method for making the composition. Also provided are low and high overbased sulfonates made from the mixture of polyalkenyl sulfonic acids, and lubricating oils containing the sulfonates.

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PAJ, WPI Data, EP0-Internal

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5 408 018 A (H. P. RATH) 18 April 1995 (1995-04-18) cited in the application column 1, line 7 -column 2, line 10 column 2, line 44 -column 3, line 18 column 8, line 53 -column 10, line 48 column 10, line 66 -column 11, line 5; claims 1-12 ---	1-88
Y	US 5 448 000 A (P. GULLAPALLI) 5 September 1995 (1995-09-05) the whole document ---	1-88
Y	EP 0 630 917 A (EXXON RESEARCH AND ENGINEERING COMPANY) 28 December 1994 (1994-12-28) the whole document ---	1-88
		-/-

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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**C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT**

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 640 626 A (ROHM AND HAAS COMPANY) 1 March 1995 (1995-03-01) claims 1-7 ----	1
A	DE 195 08 656 A (BASF AG) 19 September 1996 (1996-09-19) claims 1-17 ----	1
A	EP 0 641 810 A (BASF AG) 8 March 1995 (1995-03-08) claims 1-13 ----	1
A	EP 0 217 618 A (EXXON RESEARCH AND ENGINEERING COMPANY) 8 April 1987 (1987-04-08) claims 1-17 ----	1

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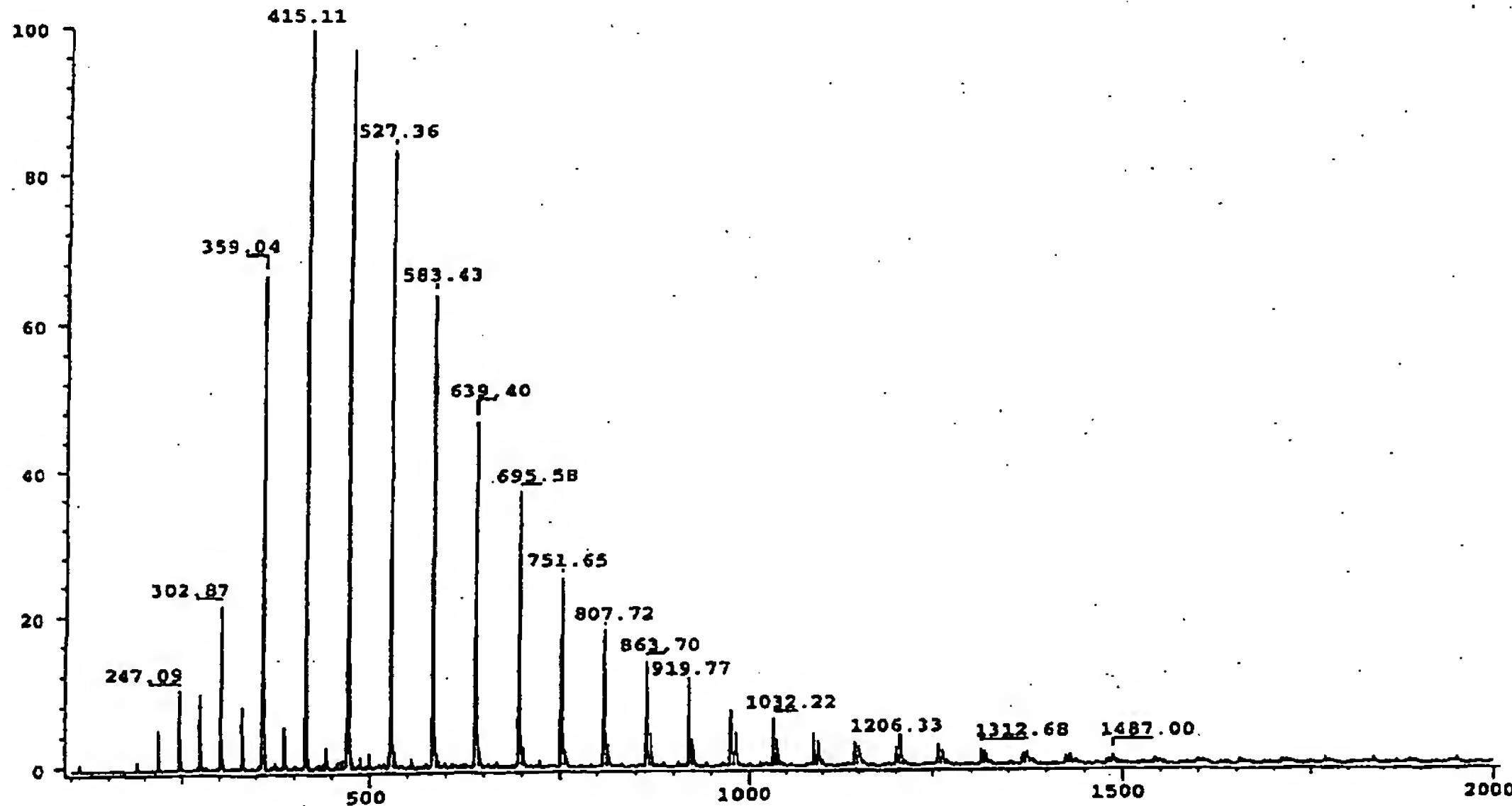
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(54) Title: POLYALKENYL SULFONATES



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(57) Abstract: Provided is a polyalkenyl sulfonic acid composition comprising a mixture of polyalkenyl sulfonic acids derived from a mixture of polyalkenes comprising greater than 20 mole percent alkyl vinylidene and 1,1-dialkyl isomers, and a method for making the composition. Also provided are low and high overbased sulfonates made from the mixture of polyalkenyl sulfonic acids, and lubricating oils containing the sulfonates.

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# **POLYALKENYL SULFONATES**

## **BACKGROUND OF THE INVENTION**

Sulfonates are a class of chemicals used in household, industrial, and institutional cleaning applications, personal care and agricultural products, metalworking fluids, industrial processes, emulsifying agents, corrosion inhibitors and as additives in lubricating oils. Some of the desirable properties of sulfonates for use in lubricating oil applications include their low cost, compatibility, water tolerance, corrosion inhibition, emulsion performance, friction properties, high temperature stability, rust performance, and light color.

10 Sulfonates that are used in lubricating oil applications have been classified as  
11 either neutral sulfonates, low overbased (LOB) sulfonates, or high overbased (HOB)  
12 sulfonates.

13 In the past, natural sulfonates, made as a by-product of white oil and process  
14 oil production, dominated the sulfonate market. However, as refineries switched to  
15 hydrotreating processes, which gave improved yields of process oils and white oils,  
16 and as the desire for higher utilization of raw materials and thus improved economics  
17 grew, synthetic sulfonates have become more readily available. Many synthetic  
18 sulfonates have been produced from sulfonated polyalkyl aromatic compounds.  
19 Unfortunately, many synthetic sulfonates provide properties that are inferior to the  
20 properties of the natural sulfonates. Thus, there is a need for low cost synthetic  
21 sulfonates that have good performance properties and can serve as a replacement for  
22 the natural sulfonates.

## SUMMARY OF THE INVENTION

25 The present invention provides a polyalkenyl sulfonic acid composition  
26 comprising a mixture of polyalkenyl sulfonic acids derived from a mixture of  
27 polyalkenes comprising greater than 20 mole percent alkyl vinylidene and 1,1-dialkyl  
28 isomers. The present invention also provides such a composition wherein the alkyl  
29 vinylidene isomer is a methyl vinylidene isomer, and the 1,1-dialkyl isomer is a 1,1-  
30 dimethyl isomer. Also provided is such a composition wherein the number average  
31 molecular weight of the polyalkene is about 168 to about 5000. In a preferred  
32 embodiment, the polyalkene is polyisobutene. In another preferred embodiment, the

1 polyalkene is polyisobutene and the molecular weight distribution of the  
2 polyisobutenyl sulfonic acids has at least 80% of the polyisobutenyl sulfonic acids  
3 molecular weights separated by even multiples of 56 daltons. The present invention  
4 further provides such a composition wherein the polyalkene is polyisobutene and less  
5 than 20% of the polyisobutenyl sulfonic acids in the molecular weight distribution of  
6 the polyisobutenyl sulfonic acids contain a total number of carbon atoms that is not  
7 evenly divisible by four.

8 Also provided by the present invention is an improved method of making  
9 polyalkenyl sulfonic acid by sulfonating polyalkenes, wherein the improvement  
10 comprises using as the polyalkenes a mixture of polyalkenes comprising greater than  
11 20 mole percent alkyl vinylidene and 1,1-dialkyl isomers. The present invention  
12 further provides the product of this process.

13 The present invention further provides a polyalkenyl sulfonate composition  
14 having a TBN of about 0 to about 60 wherein the polyalkenyl sulfonate is an alkali  
15 metal or alkaline earth metal salt of a polyalkenyl sulfonic acid derived from a mixture  
16 of polyalkenes comprising greater than 20 mole percent alkyl vinylidene and 1,1-  
17 dialkyl isomers. Further provided in accordance with this invention is a polyalkenyl  
18 sulfonate composition having a TBN of greater than 60 to about 400 wherein the  
19 polyalkenyl sulfonate is an alkali metal or alkaline earth metal salt of a polyalkenyl  
20 sulfonic acid derived from a mixture of polyalkenes comprising greater than 20 mole  
21 percent alkyl vinylidene and 1,1-dialkyl isomers.

22 In accordance with the present invention there is also provided an improved  
23 method of making polyalkenyl sulfonate by sulfonating polyalkenes and reacting the  
24 resulting polyalkenyl sulfonic acid with an alkali metal or alkaline earth metal, the  
25 improvement comprising using as the polyalkenes a mixture of polyalkenes  
26 comprising greater than 20 mole percent alkyl vinylidene and 1,1-dialkyl isomers.  
27 The present invention also provides the product produced by this process.

28 Also provided by the present invention is a lubricating oil composition  
29 comprising a major amount of an oil of lubricating viscosity and a minor amount of a  
30 polyalkenyl sulfonate composition having a TBN of about 0 to about 60 wherein the  
31 polyalkenyl sulfonate is an alkali metal or alkaline earth metal salt of a polyalkenyl  
32 sulfonic acid derived from a mixture of polyalkenes comprising greater than 20 mole

1 percent alkyl vinylidene and 1,1-dialkyl isomers. The present invention also provides  
2 a lubricating oil composition comprising a major amount of an oil of lubricating  
3 viscosity and a minor amount of a polyalkenyl sulfonate composition having a TBN of  
4 greater than 60 to about 400 wherein the polyalkenyl sulfonate is an alkali metal or  
5 alkaline earth metal salt of a polyalkenyl sulfonic acid derived from a mixture of  
6 polyalkenes comprising greater than 20 mole percent alkyl vinylidene and 1,1-dialkyl  
7 isomers.

8

9 BRIEF DESCRIPTION OF THE DRAWINGS

10 Figure 1 is a negative ion electrospray ionization mass spectrum of a  
11 polybutene sulfonic acid of a polybutenyl sulfonic acid made in accordance with the  
12 present invention.

13 Figure 2 is a negative ion electrospray ionization mass spectrum of a  
14 polybutene sulfonic acid made from a polybutene with less than 10%  
15 methylvinylidene isomer content, i.e., not a polybutenyl sulfonic acid of this  
16 invention.

17

18 DETAILED DESCRIPTION OF THE INVENTION

19 The polyalkenyl sulfonic acids of this invention are prepared by reacting a  
20 mixture of polyalkenes comprising greater than 20 mole percent alkyl vinylidene and  
21 1,1-dialkyl isomers with a source of sulfur trioxide  $-\text{SO}_3-$ . The source of  $-\text{SO}_3-$  can be  
22 a mixture of sulfur trioxide and air, sulfur trioxide hydrates, sulfur trioxide amine  
23 complexes, sulfur trioxide ether complexes, sulfur trioxide phosphate complexes,  
24 acetyl sulfate, a mixture of sulfur trioxide and acetic acid, sulfamic acid, alkyl sulfates  
25 or chlorosulfonic acid. The reaction may be conducted neat or in any inert anhydrous  
26 solvent. The conditions for sulfonation are not critical. Reaction temperatures can  
27 range from -30°C. to 200°C. and depends on the particular sulfonating agent  
28 employed. For example, acetyl sulfate requires low temperatures for reaction and  
29 elevated temperatures should be avoided to prevent decomposition of the product.  
30 Reaction time can vary from a few minutes to several hours depending on other  
31 conditions, such as reaction temperature. The extent of the reaction can be determined

1 by titration of sulfonated polyalkene after any free sulfuric acid has been washed out.  
2 Typical mole ratios of sulfonating agent to polyalkene can be about 1:1 to 2:1.

3 The preferred sulfonating agent is acetyl sulfate (or a mixture of sulfuric acid  
4 and acetic anhydride which forms acetyl sulfate *in situ*) which produces the  
5 polyalkenyl sulfonic acid directly. Other sulfonating agents, such as a mixture of  
6 sulfur trioxide and air, may produce a sulfone intermediate that needs to be hydrolyzed  
7 to the sulfonic acid. This hydrolysis step can be very slow.

8 The polyalkenes used to prepare the polyalkenyl sulfonic acid are a mixture of  
9 polyalkenes having 12 to 350 carbon atoms. The mixture comprises greater than 20  
10 mole percent, preferably greater than 50 mole percent, and more preferably greater  
11 than 70 mole percent alkylvinylidene and 1,1-dialkyl isomers. The preferred  
12 alkylvinylidene isomer is a methyl vinylidene isomer, and the preferred 1,1-dialkyl  
13 isomer is a 1,1-dimethyl isomer.

14 The polyalkenes have a number average molecular weight in the range of  
15 about 168 to about 5000. Polyalkenes having number average molecular weights of  
16 about 550, 1000 or 2300 are particularly useful.

17 The preferred polyalkene is polyisobutene. Especially preferred are  
18 polyisobutenes made using  $\text{BF}_3$  as catalyst.

19 U. S. Patent No. 5,408,018, which issued on April 18, 1995 to Rath and which  
20 is incorporated by reference in its entirety, and the references cited therein describe a  
21 suitable process for the production of polyisobutenes that contain greater than 20 mole  
22 percent alkylvinylidene and 1,1-dialkyl isomers.

23 Typically, when polyisobutetyl sulfonic acids or sulfonates are prepared from  
24 polyisobutene having a low mole percent of alkylvinylidene and 1,1-dialkyl isomers,  
25 the product has a molecular weight distribution similar to that shown in Figure 2.  
26 Since polyisobutene is used to prepare the sulfonic acid or sulfonate, it should be  
27 expected that the mass spectrum of the product would show compounds separated by  
28 even multiples of 56 daltons, i.e., a  $\text{C}_4\text{H}_8$  fragment. However, Figure 2, which is the  
29 mass spectrum of a polyisobutetyl sulfonate prepared from a polyisobutene having a  
30 mole percent of methylvinylidene isomers of less than 20%, clearly shows compounds  
31 which are separated by less than 56 daltons.

1        It has now been discovered that when polyisobutene having a mole percent of  
2        alkyl vinylidene and 1,1-dialkyl isomers greater than 20% is used to prepare  
3        polyisobutenyl sulfonic acids or sulfonates, the molecular weight distribution of the  
4        resulting product has at least 80% of the polyisobutenyl sulfonic acids or sulfonates  
5        whose molecular weights are separated by even multiples of 56 daltons (see Figure 1).  
6        In other words, less than 20% of the polyisobutenyl sulfonic acids or sulfonates in the  
7        molecular weight distribution of the sulfonic acids or sulfonates contain a total  
8        number of carbon atoms that is not evenly divisible by four.

9        The polyalkenyl sulfonates of this invention are prepared by reacting the  
10      polyalkenyl sulfonic acid (prepared as described above) with a source of an alkali or  
11      alkaline earth metal. The alkali or alkaline earth metal can be introduced into the  
12      sulfonate by any suitable means. One method comprises combining a basically  
13      reacting compound of the metal, such as the hydroxide, with the polyalkenyl sulfonic  
14      acid. This is generally carried out in the presence of a hydroxylic promoter such as  
15      water, alcohols such as 2-ethyl hexanol, methanol or ethylene glycol, and an inert  
16      solvent for the sulfonate, typically with heating. Under these conditions, the basically  
17      reacting compound will yield the metal sulfonate. The hydroxylic promoter and  
18      solvent can then be removed to yield the metal sulfonate.

19       Under certain circumstances, it may be more convenient to prepare an alkali  
20      metal polyalkenyl sulfonate and convert this material by metathesis into an alkaline  
21      earth metal sulfonate. Using this method, the sulfonic acid is combined with a basic  
22      alkali metal compound such as sodium or potassium hydroxide. The sodium or  
23      potassium sulfonate obtained can be purified by aqueous extraction. Then, the sodium  
24      or potassium sulfonate is combined with an alkaline earth metal salt to form the  
25      alkaline earth metal sulfonate. The most commonly used alkaline earth metal  
26      compound is a halide, particularly a chloride. Typically, the sodium or potassium  
27      sulfonate is combined with an aqueous chloride solution of the alkaline earth metal  
28      and stirred for a time sufficient for metathesis to occur. Thereafter, the water phase is  
29      removed and the solvent may be evaporated, if desired.

30       The preferred sulfonates are alkaline earth metal sulfonates, especially those of  
31      calcium, barium and magnesium. Most preferred are the calcium and magnesium  
32      sulfonates.

1        The polyalkenyl sulfonates of this invention are either neutral or overbased  
2        sulfonates. Overbased materials are characterized by a metal content in excess of that  
3        which would be present according to the stoichiometry of the metal cation in the  
4        sulfonate said to be overbased. Thus, a monosulfonic acid when neutralized with an  
5        alkaline earth metal compound, such as a calcium compound, will produce a normal  
6        sulfonate containing one equivalent of calcium for each equivalent of acid. In other  
7        words, the normal metal sulfonate will contain one mole of calcium for each two  
8        moles of the monosulfonic acid.

9        By using well known procedures, overbased or basic complexes of the sulfonic  
10      acid can be obtained. These overbased materials contain amounts of metal in excess  
11      of that required to neutralize the sulfonic acid. Highly overbased sulfonates can be  
12      prepared by the reaction of overbased sulfonates with carbon dioxide under reaction  
13      conditions. A discussion of the general methods for preparing overbased sulfonates  
14      and other overbased products is disclosed in U. S. Patent No. 3,496,105, issued  
15      February 17, 1970 to LeSuer, which is incorporated by reference in its entirety.

16      The amount of overbasing can be expressed as a Total Base Number ("TBN"),  
17      which refers to the amount of base equivalent to one milligram of KOH in one gram  
18      of sulfonate. Thus, higher TBN numbers reflect more alkaline products and therefore a  
19      greater alkalinity reserve. The TBN for a composition is readily determined by ASTM  
20      test method D664 or other equivalent methods. The overbased polyalkenyl sulfonates  
21      of this invention can have relatively low TBN, i.e., about 0 to about 60, or relatively  
22      high TBN, i.e., greater than 60 to about 400.

23      The polyalkenyl sulfonates of this invention are useful as additives in  
24      lubricating oils. They have good tolerance to water, a light color and provide good  
25      performance characteristics.

26      The lubricating oil compositions of this invention comprise a major amount of  
27      an oil of lubricating viscosity and a minor amount of the polyalkenyl sulfonates of this  
28      invention. The oils can be derived from petroleum or be synthetic. The oils can be  
29      paraffinic, naphthenic, halosubstituted hydrocarbons, synthetic esters, or combinations  
30      thereof. Oils of lubricating viscosity have viscosities in the range from 35 to 55,000  
31      SUS at 100°F., and more usually from about 50 to 10,000 SUS at 100°F. The  
32      lubricating oil compositions contain an amount of the polyalkenyl sulfonates of this

1 invention sufficient to provide dispersant properties, typically from about 0.1 weight  
2 percent to 10 weight percent, preferably from about 0.5 weight percent to about 7  
3 weight percent.

4 Other conventional additives that can be used in combination with the  
5 polyalkenyl sulfonates of this invention include oxidation inhibitors, antifoam agents,  
6 viscosity index improvers, pour point depressants, dispersants and the like.

7 The lubricating oil compositions of this invention are useful for lubricating  
8 internal combustion engines and automatic transmissions, and as industrial oils such  
9 as hydraulic oils, heat transfer oils, torque fluids, etc.

10

11

#### EXAMPLE 1

##### 12 PREPARATION OF A POLYISOBUTENE SULFONIC ACID FROM A 13 HIGH METHYLVINYLDENE POLYISOBUTENE THAT HAS 14 A $M_n$ OF 550 AND ACETYL SULFATE

15 To a beaker is added 5.5g (0.01 mol) of Glissopal 550 polyisobutene (which  
16 has greater than about 80% methylvinylidene content with a number average  
17 molecular weight of about 550) dissolved in 20mL hexane. To this is added 1.63g  
18 acetic anhydride (0.016 mole) and then 0.98g sulfuric acid (0.01 mole). The resulting  
19 mixture is stirred at room temperature for one hour. Then some methanol is added to  
20 quench the reaction and the solvents are removed in vacuo. A total of 7.16g of crude  
21 polyisobutene sulfonic acid is obtained.

22

#### EXAMPLE 2

##### 23 PREPARATION OF A LOB POLYISOBUTENE SODIUM SULFONATE 24 FROM THE PRODUCT OF EXAMPLE 1

25 To 5.91g of the sulfonic acid from Example 1 is added 20 mL isopropyl  
26 alcohol and 1 g sodium hydroxide in 1 mL of water. The resulting mixture is refluxed  
27 for 6 hours and then held at room at room temperature overnight. Two layers form  
28 and the bottom layer is decanted. The top layer contains sodium polyisobutene  
29 sulfonate (5.67g) which contains 88% actives. The lower layer is stripped in vacuo  
30 and contains 1.14g of a mixture of sodium hydroxide and sodium polyisobutene  
31 sulfonate.

1

EXAMPLE 3

2

## PREPARATION OF CALCIUM LOB POLYISOBUTENE SULFONATE

3

To a 2L round bottom flask is added 500g of Glissopal 550 polyisobutene (0.91 mol), 140.3g acetic anhydride (1.38 mol), and 84.7g concentrated sulfuric acid (0.86 mol) at room temperature. The resulting mixture is stirred 4 hours at room temperature. Then to this mixture is added 50 mL methanol to quench the reaction, and 500g of 100 neutral diluent oil. To this is then added 32.0g calcium hydroxide (0.43 mol) and 20 mL water. The resulting mixture is heated to 175°F and then 100 mL water is added. This is then heated to 225-230°F for 30 minutes, and then heated at 330°F for 1 hour to strip off the water. A calcium polyisobutene sulfonate is obtained.

11

EXAMPLE 4

12

PREPARATION OF POLYISOBUTENE SULFONIC ACID USING SO<sub>3</sub> AND AIR

13

A thin film of Glissopal 550 polyisobutene is sulfonated using SO<sub>3</sub> and air under the following conditions: temperature 60°C, SO<sub>3</sub> flow 16L/hr, air flow 192L/hr, feed rate 4.5g/min. The product from this reaction is a mixture of polyisobutene sulfonic acid and polyisobutene sultone. The product contains 2.04% sulfonate as calcium sulfonate and 0.70% sulfuric acid as determined by hyamine titration.

19

EXAMPLE 5

20

PREPARATION OF POLYISOBUTENE SULFONIC ACID USING SO<sub>3</sub> AND AIR

21

A thin film of Glissopal 550 polyisobutene is sulfonated using SO<sub>3</sub> and air under the following conditions: temperature 60°, SO<sub>3</sub> flow 16L/hr, air flow 192L/hr, feed rate 4.2g/min. A total of 1354g product is obtained which is a mixture of polyisobutene sulfonic acid and polyisobutene sultone. The product contains 2.5% sulfonate as calcium sulfonate and 1.02% sulfuric acid as determined by hyamine titration. The acid number is determined by the ASTM D664 test to be 59.9 mg KOH/g sample.

28

EXAMPLE 6

29

## PREPARATION OF SODIUM POLYISOBUTENE SULFONATE

30

The mixture of polyisobutene sulfonic acid and polyisobutene sultone from Example 5 is hydrolyzed using the following procedure. To a 100 mL three neck flask equipped with a reflux condenser and stirrer is added 20g of polyisobutene

1 sulfonic acid and the resulting mixture is heated to 100°C. To this is added 5 mL 49%  
2 sodium hydroxide solution and the resulting mixture is stirred for four hours. The  
3 product from this reaction is a mixture of sodium polyisobutene sulfonate and  
4 polyisobutene sultone.

5 EXAMPLE 7

6 PREPARATION OF CALCIUM POLYISOBUTENE SULFONATE  
7 FROM 550 MW POLYISOBUTENE (NEUTRAL SULFONATE)

8 To a 2 L round bottom flask is added 500g (0.91 mol) Glissopal 550 (550 M<sub>n</sub>)  
9 polyisobutene containing about 85% methylvinylidene isomer), 140.3 g acetic  
10 anhydride, (1.38 mol; 1.5 equivalents), and 84.7g sulfuric acid (0.864 mol; 0.95  
11 equivalents) dropwise at room temperature. The resulting mixture is stirred 4 hours  
12 at room temperature. Then to this is added 50 mL methanol and then 500g 100  
13 neutral diluent oil is added. To this is then added 32.0g calcium hydroxide (0.43 mol)  
14 and 20 mL water. This is heated to about 80°C and an additional 100 mL of water is  
15 added. Then the volatile materials are removed at elevated temperatures. The product  
16 is filtered to give 842.3 g of product which has a TBN of 3.4 mg KOH/g sample, a  
17 viscosity @100°C of 72.4 cSt., 1.50% Ca, and 2.31% S.

18 EXAMPLE 8

19 PREPARATION OF CALCIUM POLYISOBUTENE SULFONATE  
20 FROM 550 MW POLYISOBUTENE (LOB SULFONATE)

21 To a 4 L beaker is added 500g (0.91 mol) Glissopal 550 polyisobutene (550  
22 M<sub>n</sub>) polyisobutene with about 85% methylvinylidene isomer content), 140.3 g acetic  
23 anhydride (1.38 mol), and 84.7g sulfuric acid (0.864 mol). The resulting mixture is  
24 stirred 1 hour at room temperature. To this is then added 50 mL methanol, 500g 100  
25 neutral diluent oil, and 100 mL water. The resulting mixture is heated to 190°F and  
26 48g (0.649 mol) calcium hydroxide is added. This is stirred for one hour and then the  
27 temperature is raised to 212°F and maintained there until all the volatile material has  
28 distilled. The resulting product is then filtered to give a LOB calcium polyisobutene  
29 sulfonate which has a TBN of 12.3 mg KOH/g sample, 2.24 % S, 1.85% Ca, and a  
30 viscosity @ 100°C of 79.4 cSt.

1

EXAMPLE 9

## 2 PREPARATION OF ADDITIONAL POLYISOBUTENE SULFONATES

3 Additional examples of calcium polyisobutene sulfonates are carried out using  
 4 different conditions, charge mole ratios ("CMR's") and polyisobutene ("PIB")  
 5 molecular weights as shown in Table 1.

6

Ex.	PIB $M_n$	% diluent oil	Ac <sub>2</sub> O / PIB	H <sub>2</sub> SO <sub>4</sub> / PIB	H <sub>2</sub> SO <sub>4</sub> / Ca(OH) <sub>2</sub>	% Ca	% S	TBN	Vis @ 100°C
7	550	50	1.52	0.95	2.01	1.50	2.31	3.4	72.4
8	550	50	1.52	0.95	1.33	1.85	2.24	12.0	79.4
9	550	45	1.51	0.95	1.83	1.84	2.60	5.5	113.8
10	550	45	1.51	0.95	2.00	1.71	2.58	2.6	167.4
11	1000	45	1.51	0.95	1.81	1.08	1.50	3.1	153.8
12	1000	45	1.51	0.95	1.76	1.03	1.52	0.9	156.1
13	1000	45	1.50	0.95	1.83	1.08	1.49	3.9	163.8

7

EXAMPLE 149 PREPARATION OF CALCIUM ACETATE-FREE 550  $M_n$   
10 CALCIUM POLYISOBUTENE SULFONATE

11 The sulfonic acid from 550  $M_n$  polyisobutene is first prepared by reacting  
 12 Glissopal 550 polyisobutene (2000 g, 3.64 mol), with 408.3 g acetic anhydride (4.0  
 13 mol), and 338.7 g sulfuric acid (3.46 mol). The resulting mixture is stirred for one  
 14 hour at room temperature. Then 200 mL of methanol is added. The resulting product  
 15 contains about 90% actives. Then 260 g of this product is diluted with 260 g of 100  
 16 neutral diluent oil and this is heated at 40°C with a nitrogen sparge to remove the  
 17 unreacted acetic acid, methyl acetate, and methanol. Analysis by <sup>1</sup>H NMR  
 18 spectroscopy indicates that only about 0.3% acetic acid remained. This product  
 19 (448.2 g) is then placed in a 1000 mL beaker and heated to 190°F and to this is added  
 20 13.2g calcium hydroxide. The resulting mixture is stirred for 1 hour at 190°F, and  
 21 then the temperature is increased to 330°F to remove any volatile material. The  
 22 resulting product is then filtered to give a calcium acetate-free calcium polyisobutene

1 sulfonate which has a TBN of 5.4 mg KOH/g sample, 1.12%Ca, 1.82% S, and a  
2 viscosity @ 100°C of 27.5 cSt.

3 COMPARATIVE EXAMPLE A

4 PREPARATION OF 950 M<sub>n</sub> POLYISOBUTENE SULFONIC ACID  
5 FROM PARAPOL 1000

6 200g Parapol 950 (950 M<sub>n</sub> polyisobutene with less than 5% methylvinylidene  
7 isomer content, 0.21 mol) is reacted with 22.46g acetic anhydride (0.22 mol) and  
8 18.63g sulfuric acid (0.190 mol). The resulting product is stirred at room temperature  
9 for 1 hour then 20 mL methanol was added. This product contains only about 67%  
10 actives.

11 EXAMPLE 15

12 PREPARATION OF 1000 M<sub>n</sub> POLYISOBUTENE SULFONIC ACID  
13 FROM GLISSOPAL 1000

14 To 2000g (2.0 mol) of Glissopal 1000 polyisobutene (M<sub>n</sub> 1000 with about  
15 85% methylvinylidene isomer content) is added 224.6 g acetic anhydride (2.2 mol)  
16 and 186.3 g of sulfuric acid (1.90 mol). The resulting product is reacted as in  
17 Comparative Example A. The product contains about 90% actives. This shows the  
18 improvement in yield that is obtained with the teachings of this invention.

19 COMPARATIVE EXAMPLE B

20 ELECTROSPRAY IONIZATION-MASS SPECTRUM OF SULFONIC ACID  
21 FROM POLYISOBUTENE WITH LESS THAN 20% METHYLVINYLIDENE  
22 CONTENT

23 Figure 2 shows the electrospray ionization mass spectrum of a polybutene  
24 sulfonic acid from Hivis 5 (polybutene with less than 10% methylvinylidene isomer  
25 content). The spectrum shows a molecular weight distribution with molecular ions  
26 that are separated by 14 daltons. This indicates that the polyisobutene sulfonic acid  
27 actually is not a mixture of C<sub>12</sub>, C<sub>16</sub>, C<sub>20</sub> etc. isomers, but is a mixture of C<sub>12</sub>, C<sub>13</sub>, C<sub>14</sub>,  
28 etc., isomers.

1

EXAMPLE 16

2

ELECTROSPRAY IONIZATION-MASS SPECTRUM OF SULFONIC ACID  
FROM POLYISOBUTENE WITH MORE THAN 20% METHYLVINYLDENE  
CONTENT

3

Figure 1 shows the electrospray ionization mass spectrum of a polybutene sulfonic acid from Glissopal 550 (polybutene with greater than 85% methylvinylidene isomer content). The spectrum shows a molecular weight distribution with molecular ions that are separated by 56 daltons. This indicates that the polyisobutene sulfonic acid is a mixture of C<sub>12</sub>, C<sub>16</sub>, C<sub>20</sub>, etc., isomers (i.e., the ions are multiples of four carbon atoms).

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## 1    WHAT IS CLAIMED IS:

2

3    1.    A polyalkenyl sulfonic acid composition comprising a mixture of polyalkenyl  
4    sulfonic acids derived from a mixture of polyalkenes comprising greater than  
5    20 mole percent alkyl vinylidene and 1,1-dialkyl isomers.

6

7    2.    The composition of claim 1 wherein the mixture of polyalkenes comprises  
8    greater than 50 mole percent alkyl vinylidene and 1,1-dialkyl isomers.

9

10   3.    The composition of claim 1 wherein the mixture of polyalkenes comprises  
11   greater than 70 mole percent alkyl vinylidene and 1,1-dialkyl isomers.

12

13   4.    The composition of claim 1, 2 or 3 wherein the alkyl vinylidene isomer is a  
14   methyl vinylidene isomer, and the 1,1-dialkyl isomer is a 1,1-dimethyl isomer.

15

16   5.    The composition of claim 1 wherein the number average molecular weight of  
17   the polyalkene is about 168 to about 5000.

18

19   6.    The composition of claim 1 wherein the number average molecular weight of  
20   the polyalkene is about 550.

21

22   7.    The composition of claim 1 wherein the number average molecular weight of  
23   the polyalkene is about 1000.

24

25   8.    The composition of claim 1 wherein the number average molecular weight of  
26   the polyalkene is about 2300.

27

28   9.    The composition of claim 1 wherein the polyalkene is polyisobutene.

29

30   10.   The composition of claim 9 wherein the polyisobutene is made using a  $\text{BF}_3$   
31   catalyst.

32

- 1 11. The composition of claim 1 wherein the polyalkene is polyisobutene and the  
2 molecular weight distribution of the polyisobutenyl sulfonic acids has at least  
3 80% of the polyisobutenyl sulfonic acids molecular weights separated by even  
4 multiples of 56 daltons.
- 5
- 6 12. The composition of claim 1 wherein the polyalkene is polyisobutene and less  
7 than 20% of the polyisobutenyl sulfonic acids in the molecular weight  
8 distribution of the polyisobutenyl sulfonic acids contain a total number of  
9 carbon atoms that is not evenly divisible by four.
- 10
- 11 13. In a method of making polyalkenyl sulfonic acid by sulfonating polyalkenes,  
12 the improvement comprising using as the polyalkenes a mixture of polyalkenes  
13 comprising greater than 20 mole percent alkyl vinylidene and 1,1-dialkyl  
14 isomers.
- 15
- 16 14. The method of claim 13 wherein the mixture of polyalkenes comprises greater  
17 than 50 mole percent alkyl vinylidene and 1,1-dialkyl isomers.
- 18
- 19 15. The method of claim 13 wherein the mixture of polyalkenes comprises greater  
20 than 70 mole percent alkyl vinylidene and 1,1-dialkyl isomers.
- 21
- 22 16. The method of claim 13, 14 or 15 wherein the alkyl vinylidene isomer is a  
23 methyl vinylidene isomer, and the 1,1-dialkyl isomer is a 1,1-dimethyl isomer.
- 24
- 25 17. The method of claim 13 wherein the number average molecular weight of the  
26 polyalkene is about 168 to about 5000.
- 27
- 28 18. The method of claim 13 wherein the number average molecular weight of the  
29 polyalkene is about 550.
- 30
- 31 19. The method of claim 13 wherein the number average molecular weight of the  
32 polyalkene is about 1000.

- 1 20. The method of claim 13 wherein the number average molecular weight of the
- 2 polyalkene is about 2300.
- 3
- 4 21. The method of claim 13 wherein the polyalkene is polyisobutene.
- 5
- 6 22. The method of claim 21 wherein the polyisobutene is made using a  $\text{BF}_3$
- 7 catalyst.
- 8
- 9 23. The method of claim 13 wherein the polyalkene is polyisobutene and the
- 10 molecular weight distribution of the polyisobutyl sulfonic acids has at least
- 11 80% of the polyisobutyl sulfonic acids molecular weights separated by even
- 12 multiples of 56 daltons.
- 13
- 14 24. The method of claim 13 wherein the polyalkene is polyisobutene and less than
- 15 20% of the polyisobutyl sulfonic acids in the molecular weight distribution
- 16 of the polyisobutyl sulfonic acids contain a total number of carbon atoms
- 17 that is not evenly divisible by four.
- 18
- 19 25. The product produced by the method of claim 13, 14, 15, 17, 18, 19, 20, 21,
- 20 22, 23 or 24.
- 21
- 22 26. The product produced by the method of claim 16.
- 23
- 24 27. A polyalkenyl sulfonate composition having a TBN of about 0 to about 60
- 25 wherein the polyalkenyl sulfonate is an alkali metal or alkaline earth metal salt
- 26 of a polyalkenyl sulfonic acid derived from a mixture of polyalkenes
- 27 comprising greater than 20 mole percent alkyl vinylidene and 1,1-dialkyl
- 28 isomers.
- 29
- 30 28. The composition of claim 27 wherein the mixture of polyalkenes comprises
- 31 greater than 50 mole percent alkyl vinylidene and 1,1-dialkyl isomers.
- 32

- 1 29. The composition of claim 27 wherein the mixture of polyalkenes comprises  
2 greater than 70 mole percent alkyl vinylidene and 1,1-dialkyl isomers.  
3
- 4 30. The composition of claim 27, 28 or 29 wherein the alkyl vinylidene isomer is a  
5 methyl vinylidene isomer, and the 1,1-dialkyl isomer is a 1,1-dimethyl isomer.  
6
- 7 31. The composition of claim 27 wherein the number average molecular weight of  
8 the polyalkene is about 168 to about 5000.  
9
- 10 32. The composition of claim 27 wherein the number average molecular weight of  
11 the polyalkene is about 550.  
12
- 13 33. The composition of claim 27 wherein the number average molecular weight of  
14 the polyalkene is about 1000.  
15
- 16 34. The composition of claim 27 wherein the number average molecular weight of  
17 the polyalkene is about 2300.  
18
- 19 35. The composition of claim 27 wherein the polyalkene is polyisobutene.  
20
- 21 36. The composition of claim 35 wherein the polyisobutene is made using a  $\text{BF}_3$   
22 catalyst.  
23
- 24 37. The composition of claim 27 wherein the polyalkene is polyisobutene and the  
25 molecular weight distribution of the polyisobutyl sulfonic acids has at least  
26 80% of the polyisobutyl sulfonic acids molecular weights separated by even  
27 multiples of 56 daltons.  
28
- 29 38. The composition of claim 27 wherein the polyalkene is polyisobutene and less  
30 than 20% of the polyisobutyl sulfonic acids in the molecular weight  
31 distribution of the polyisobutyl sulfonic acids contain a total number of  
32 carbon atoms that is not evenly divisible by four.

1 39. A polyalkenyl sulfonate composition having a TBN of greater than 60 to about  
2 400 wherein the polyalkenyl sulfonate is an alkali metal or alkaline earth metal  
3 salt of a polyalkenyl sulfonic acid derived from a mixture of polyalkenes  
4 comprising greater than 20 mole percent alkyl vinylidene and 1,1-dialkyl  
5 isomers.

6

7 40. The composition of claim 39 wherein the mixture of polyalkenes comprises  
8 greater than 50 mole percent alkyl vinylidene and 1,1-dialkyl isomers.

9

10 41. The composition of claim 39 wherein the mixture of polyalkenes comprises  
11 greater than 70 mole percent alkyl vinylidene and 1,1-dialkyl isomers.

12

13 42. The composition of claim 39, 40 or 41 wherein the alkyl vinylidene isomer is a  
14 methyl vinylidene isomer, and the 1,1-dialkyl isomer is a 1,1-dimethyl isomer.

15

16 43. The composition of claim 39 wherein the number average molecular weight of  
17 the polyalkene is about 168 to about 5000.

18

19 44. The composition of claim 39 wherein the number average molecular weight of  
20 the polyalkene is about 550.

21

22 45. The composition of claim 39 wherein the number average molecular weight of  
23 the polyalkene is about 1000.

24

25 46. The composition of claim 39 wherein the number average molecular weight of  
26 the polyalkene is about 2300.

27

28 47. The composition of claim 39 wherein the polyalkene is polyisobutene.

29

30 48. The composition of claim 47 wherein the polyisobutene is made using a  $\text{BF}_3$   
31 catalyst.

32

1 49. The composition of claim 39 wherein the polyalkene is polyisobutene and the  
2 molecular weight distribution of the polyisobutenyl sulfonic acids has at least  
3 80% of the polyisobutenyl sulfonic acids molecular weights separated by even  
4 multiples of 56 daltons.

5

6 50. The composition of claim 39 wherein the polyalkene is polyisobutene and less  
7 than 20% of the polyisobutenyl sulfonic acids in the molecular weight  
8 distribution of the polyisobutenyl sulfonic acids contain a total number of  
9 carbon atoms that is not evenly divisible by four.

10

11 51. In a method of making polyalkenyl sulfonate by sulfonating polyalkenes and  
12 reacting the resulting polyalkenyl sulfonic acid with an alkali metal or alkaline  
13 earth metal, the improvement comprising using as the polyalkenes a mixture of  
14 polyalkenes comprising greater than 20 mole percent alkyl vinylidene and  
15 1,1-dialkyl isomers.

16

17 52. The method of claim 51 wherein the mixture of polyalkenes comprises greater  
18 than 50 mole percent alkyl vinylidene and 1,1-dialkyl isomers.

19

20 53. The method of claim 51 wherein the mixture of polyalkenes comprises greater  
21 than 70 mole percent alkyl vinylidene and 1,1-dialkyl isomers.

22

23 54. The method of claim 51, 52 or 53 wherein the alkyl vinylidene isomer is a  
24 methyl vinylidene isomer, and the 1,1-dialkyl isomer is a 1,1-dimethyl isomer.

25

26 55. The method of claim 51 wherein the number average molecular weight of the  
27 polyalkene is about 168 to about 5000.

28

29 56. The method of claim 51 wherein the number average molecular weight of the  
30 polyalkene is about 550.

31

1 57. The method of claim 51 wherein the number average molecular weight of the  
2 polyalkene is about 1000.

3

4 58. The method of claim 51 wherein the number average molecular weight of the  
5 polyalkene is about 2300.

6

7 59. The method of claim 51 wherein the polyalkene is polyisobutene.

8

9 60. The method of claim 59 wherein the polyisobutene is made using a  $\text{BF}_3$   
10 catalyst.

11

12 61. The method of claim 51 wherein the polyalkene is polyisobutene and the  
13 molecular weight distribution of the polyisobutyl sulfonic acids has at least  
14 80% of the polyisobutyl sulfonic acids molecular weights separated by even  
15 multiples of 56 daltons.

16

17 62. The method of claim 51 wherein the polyalkene is polyisobutene and less than  
18 20% of the polyisobutyl sulfonic acids in the molecular weight distribution  
19 of the polyisobutyl sulfonic acids contain a total number of carbon atoms  
20 that is not evenly divisible by four.

21

22 63. The product produced by the method of claim 51, 52, 53, 55, 56, 57, 58, 59,  
23 60, 61 or 62.

24

25 64. The product produced by the method of claim 54.

26

27 65. A lubricating oil composition comprising a major amount of an oil of  
28 lubricating viscosity and a minor amount of a polyalkenyl sulfonate  
29 composition having a TBN of about 0 to about 60 wherein the polyalkenyl  
30 sulfonate is an alkali metal or alkaline earth metal salt of a polyalkenyl  
31 sulfonic acid derived from a mixture of polyalkenes comprising greater than  
32 20 mole percent alkyl vinylidene and 1,1-dialkyl isomers.

- 1 66. The composition of claim 65 wherein the mixture of polyalkenes comprises  
2 greater than 50 mole percent alkyl vinylidene and 1,1-dialkyl isomers.  
3
- 4 67. The composition of claim 65 wherein the mixture of polyalkenes comprises  
5 greater than 70 mole percent alkyl vinylidene and 1,1-dialkyl isomers.  
6
- 7 68. The composition of claim 65, 66 or 67 wherein the alkyl vinylidene isomer is a  
8 methyl vinylidene isomer, and the 1,1-dialkyl isomer is a 1,1-dimethyl isomer.  
9
- 10 69. The composition of claim 65 wherein the number average molecular weight of  
11 the polyalkene is about 168 to about 5000.  
12
- 13 70. The composition of claim 65 wherein the number average molecular weight of  
14 the polyalkene is about 550.  
15
- 16 71. The composition of claim 65 wherein the number average molecular weight of  
17 the polyalkene is about 1000.  
18
- 19 72. The composition of claim 65 wherein the number average molecular weight of  
20 the polyalkene is about 2300.  
21
- 22 73. The composition of claim 65 wherein the polyalkene is polyisobutene.  
23
- 24 74. The composition of claim 73 wherein the polyisobutene is made using a  $\text{BF}_3$   
25 catalyst.  
26
- 27 75. The composition of claim 65 wherein the polyalkene is polyisobutene and the  
28 molecular weight distribution of the polyisobutyl sulfonic acids has at least  
29 80% of the polyisobutyl sulfonic acids molecular weights separated by even  
30 multiples of 56 daltons.  
31

1 76. The composition of claim 65 wherein the polyalkene is polyisobutene and less  
2 than 20% of the polyisobutetyl sulfonic acids in the molecular weight  
3 distribution of the polyisobutetyl sulfonic acids contain a total number of  
4 carbon atoms that is not evenly divisible by four.

5

6 77. A composition comprising a major amount of an oil of lubricating viscosity  
7 and a minor amount of a polyalkenyl sulfonate composition having a TBN of  
8 greater than 60 to about 400 wherein the polyalkenyl sulfonate is an alkali  
9 metal or alkaline earth metal salt of a polyalkenyl sulfonic acid derived from a  
10 mixture of polyalkenes comprising greater than 20 mole percent alkyl  
11 vinylidene and 1,1-dialkyl isomers.

12

13 78. The composition of claim 77 wherein the mixture of polyalkenes comprises  
14 greater than 50 mole percent alkyl vinylidene and 1,1-dialkyl isomers.

15

16 79. The composition of claim 77 wherein the mixture of polyalkenes comprises  
17 greater than 70 mole percent alkyl vinylidene and 1,1-dialkyl isomers.

18

19 80. The composition of claim 75, 76 or 77 wherein the alkyl vinylidene isomer is a  
20 methyl vinylidene isomer, and the 1,1-dialkyl isomer is a 1,1-dimethyl isomer.

21

22 81. The composition of claim 77 wherein the number average molecular weight of  
23 the polyalkene is about 168 to about 5000.

24

25 82. The composition of claim 77 wherein the number average molecular weight of  
26 the polyalkene is about 550.

27

28 83. The composition of claim 77 wherein the number average molecular weight of  
29 the polyalkene is about 1000.

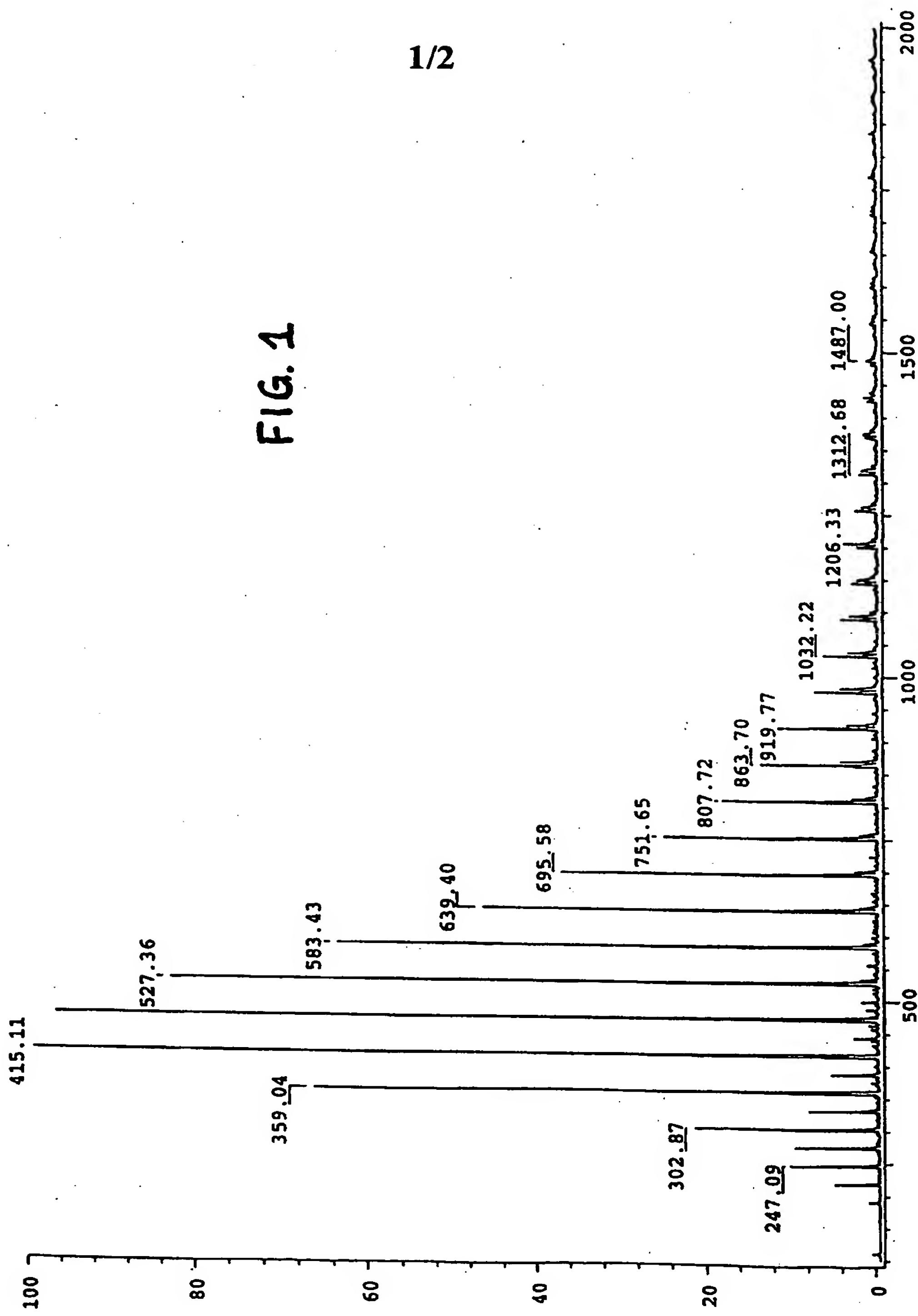
30

31 84. The composition of claim 77 wherein the number average molecular weight of  
32 the polyalkene is about 2300.

- 1 85. The composition of claim 77 wherein the polyalkene is polyisobutene.
- 2
- 3 86. The composition of claim 85 wherein the polyisobutene is made using a  $\text{BF}_3$
- 4 catalyst.
- 5
- 6 87. The composition of claim 77 wherein the polyalkene is polyisobutene and the
- 7 molecular weight distribution of the polyisobutyl sulfonic acids has at least
- 8 80% of the polyisobutyl sulfonic acids molecular weights separated by even
- 9 multiples of 56 daltons.
- 10
- 11 88. The composition of claim 77 wherein the polyalkene is polyisobutene and less
- 12 than 20% of the polyisobutyl sulfonic acids in the molecular weight
- 13 distribution of the polyisobutyl sulfonic acids contain a total number of
- 14 carbon atoms that is not evenly divisible by four.

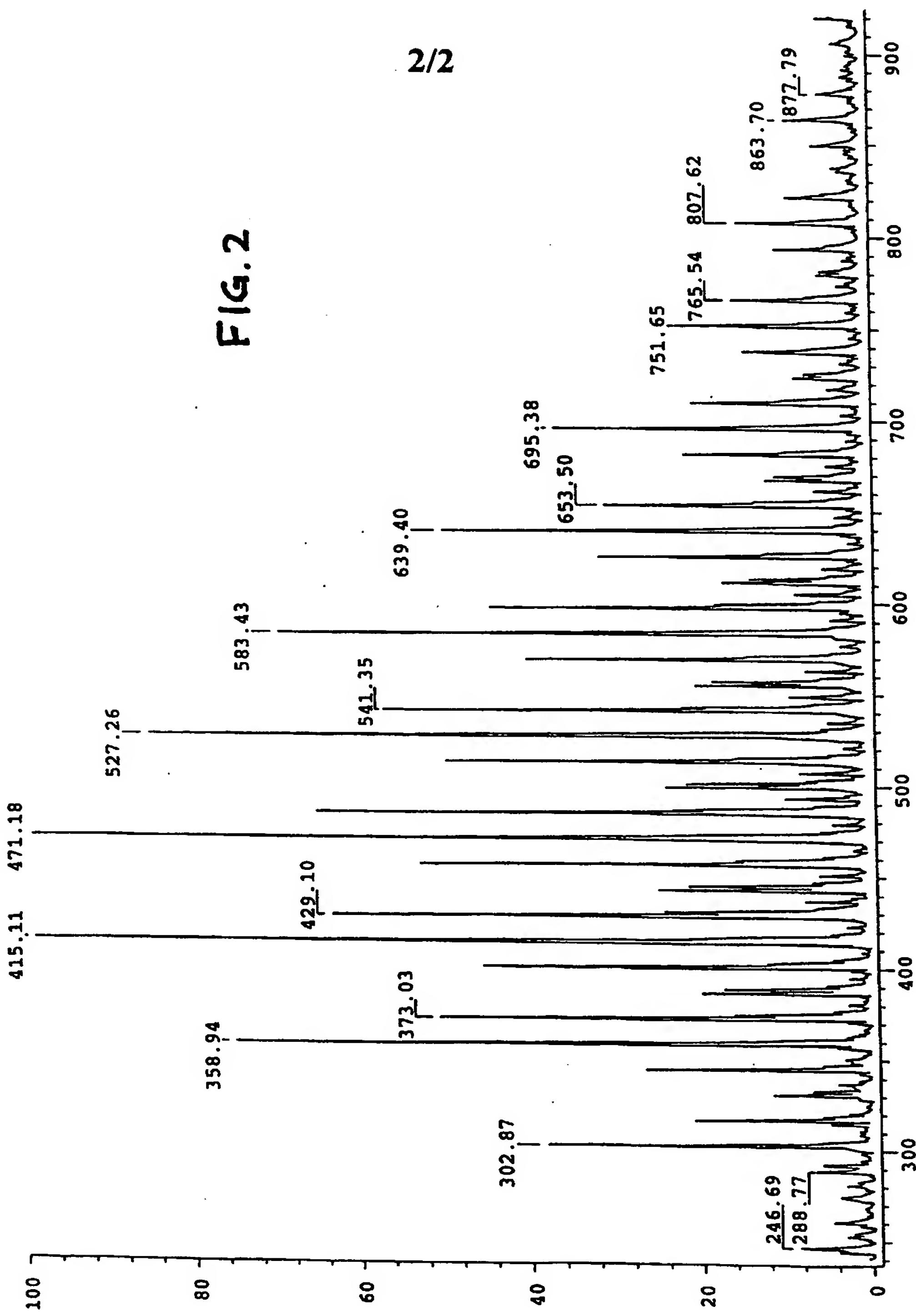
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FIG. 1



2/2

FIG. 2



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HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK,  
LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX,  
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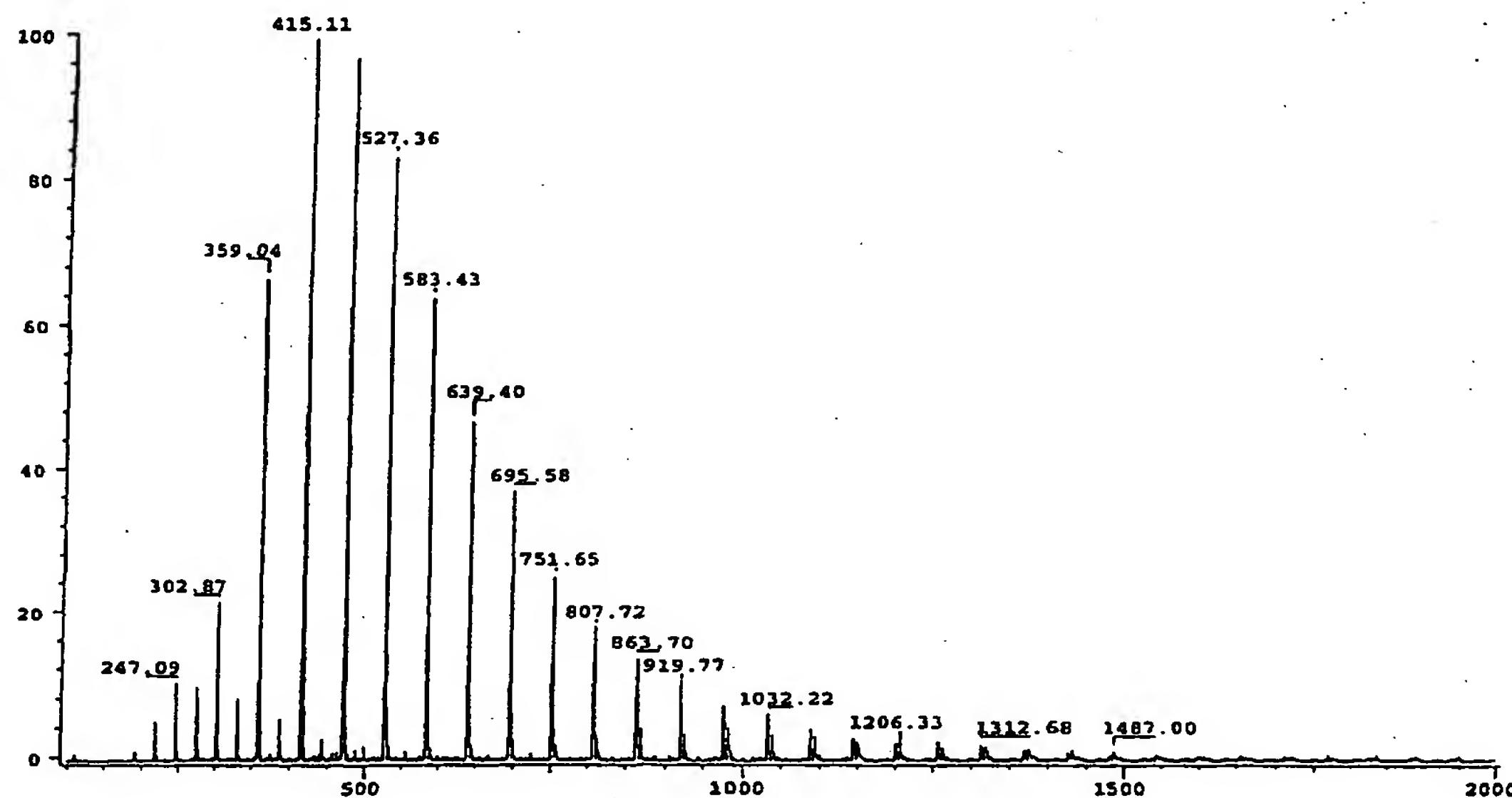
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(54) Title: POLYALKENYL SULFONATES



WO 01/70830 A3



(57) Abstract: Provided is a polyalkenyl sulfonic acid composition comprising a mixture of polyalkenyl sulfonic acids derived from a mixture of polyalkenes comprising greater than 20 mole percent alkyl vinylidene and 1,1-dialkyl isomers, and a method for making the composition. Also provided are low and high overbased sulfonates made from the mixture of polyalkenyl sulfonic acids, and lubricating oils containing the sulfonates.

**WO 01/70830 A3**

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*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

# INTERNATIONAL SEARCH REPORT

Internal Application No  
PCT/US 01/08345

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 C08F8/36 C08F8/44

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

PAJ, WPI Data, EPO-Internal

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Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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**INTERNATIONAL SEARCH REPORT**

International Application No
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**C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT**

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